EUR 379.e

EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

CORROSION STUDIES IN ORGANIC COOLANTS FOR NUCLEAR REACTORS

by

H. W. SCHLEICHER

1963

ORGEL Program

Joint Nuclear Research Center
Ispra Establishment - Italy
Materials Department - Metallurgy and Ceramics Service

Text presented
at the SECOND INTERNATIONAL CONGRESS ON METALLIC CORROSION,
NEW YORK (11-15 March 1963)

LEGAL NOTICE

This document was prepared under the sponsorship of the Commission of the European Atomic Energy Community (EURATOM).

Neither the EURATOM Commission, its contractors nor any person acting on their behalf :

1° — Make any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this document, or that the use of any information, apparatus, method, or process disclosed in this document may not infringe privately owned rights ; or

2° — Assume any liability with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this document.

This report can be obtained, at the price of Belgian Francs 60, from : PRESSES ACADEMIQUES EUROPEENNES — 98, Chaussée de Charleroi, Brussels 6.

Please remit payments :

— to BANQUE DE LA SOCIETE GENERALE (Agence Ma Campagne) — Brussels — account No 964.558,

— to BELGIAN AMERICAN BANK AND TRUST COMPANY — New York — account No 121.86,

— to LLOYDS BANK (Foreign) Ltd. — 10 Moorgate — London E.C.2,

giving the reference : « EUR 379 . e — Corrosion studies in organic coolants for nuclear reactors ».

This document was duplicated on the basis of the best available copy.

Printed by IMPRIMERIE L. VANMELLE, S.A., GHENT,
Brussels, August 1963.

E U R 3 7 9 . e

CORROSION STUDIES IN ORGANIC COOLANTS FOR NUCLEAR REACTORS by H. W. SCHLEICHER

European Atomic Energy Community — EURATOM
ORGEL Program
Joint Nuclear Research Center
Ispra Establishment (Italy)
Materials Department — Metallurgy and Ceramics Service
Text presented at the SECOND INTERNATIONAL CONGRESS ON METALLIC CORROSION, NEW YORK (11 - 15 March 1963)
Brussels, August 1963 — pages 46 — figures 7

As part of the ORGEL program, static corrosion tests in organic coolants have been carried out in the Euratom Laboratories at Ispra, and under contract, in the Laboratories of Progil (France), Istituto Sperimentale dei Metalli Leggeri (Italy) and Tréfileries et Laminoirs du Havre (France).

E U R 3 7 9 . e

CORROSION STUDIES IN ORGANIC COOLANTS FOR NUCLEAR REACTORS by H. W. SCHLEICHER

European Atomic Energy Community — EURATOM
ORGEL Program
Joint Nuclear Research Center
Ispra Establishment (Italy)
Materials Department — Metallurgy and Ceramics Service
Text presented at the SECOND INTERNATIONAL CONGRESS ON METALLIC CORROSION, NEW YORK (11 - 15 March 1963)
Brussels, August 1963 — pages 46 — figures 7

As part of the ORGEL program, static corrosion tests in organic coolants have been carried out in the Euratom Laboratories at Ispra, and under contract, in the Laboratories of Progil (France), Istituto Sperimentale dei Metalli Leggeri (Italy) and Tréfileries et Laminoirs du Havre (France).

E U R 3 7 9 . e

CORROSION STUDIES IN ORGANIC COOLANTS FOR NUCLEAR REACTORS by H. W. SCHLEICHER

European Atomic Energy Community — EURATOM
ORGEL Program
Joint Nuclear Research Center
Ispra Establishment (Italy)
Materials Department — Metallurgy and Ceramics Service
Text presented at the SECOND INTERNATIONAL CONGRESS ON METALLIC CORROSION, NEW YORK (11 - 15 March 1963)
Brussels, August 1963 — pages 46 — figures 7

As part of the ORGEL program, static corrosion tests in organic coolants have been carried out in the Euratom Laboratories at Ispra, and under contract, in the Laboratories of Progil (France), Istituto Sperimentale dei Metalli Leggeri (Italy) and Tréfileries et Laminoirs du Havre (France).

Sintered aluminium powder product of different types, carbon steel, stainless steel, magnesium, beryllium and niobium have been tested between 400° and 450° C, in autoclaves and pyrex capsules containing a mixture of terphenyls. Exposure times ranged from 24 to 2000 hours. The influence of additions of water, oxygen and chlorine has been studied.

Sintered Al, steels and Be show a good resistance to pure terphenyls, Mg is heavily oxidized and Nb can be severely hydrided. Water additions accelerate iron corrosion and chlorine enhances the corrosion of both carbon and stainless steels.

Sintered aluminium powder product of different types, carbon steel, stainless steel, magnesium, beryllium and niobium have been tested between 400° and 450° C, in autoclaves and pyrex capsules containing a mixture of terphenyls. Exposure times ranged from 24 to 2000 hours. The influence of additions of water, oxygen and chlorine has been studied.

Sintered Al, steels and Be show a good resistance to pure terphenyls, Mg is heavily oxidized and Nb can be severely hydrided. Water additions accelerate iron corrosion and chlorine enhances the corrosion of both carbon and stainless steels.

Sintered aluminium powder product of different types, carbon steel, stainless steel, magnesium, beryllium and niobium have been tested between 400° and 450° C, in autoclaves and pyrex capsules containing a mixture of terphenyls. Exposure times ranged from 24 to 2000 hours. The influence of additions of water, oxygen and chlorine has been studied.

Sintered Al, steels and Be show a good resistance to pure terphenyls, Mg is heavily oxidized and Nb can be severely hydrided. Water additions accelerate iron corrosion and chlorine enhances the corrosion of both carbon and stainless steels.

EUR 379.e

EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

CORROSION STUDIES IN ORGANIC COOLANTS FOR NUCLEAR REACTORS

by

H. W. SCHLEICHER

1963

ORGEL Program

Joint Nuclear Research Center
Ispra Establishment - Italy
Materials Department - Metallurgy and Ceramics Service

Text presented
at the SECOND INTERNATIONAL CONGRESS ON METALLIC CORROSION,
NEW YORK (11-15 March 1963)

C O N T E N T S

KEY OF THE FIGURES

KEY OF THE TABLES

CORROSION STUDIES IN ORGANIC COOLANTS FOR NUCLEAR REACTORS

SUMMARY

As part of the ORGEL program [M], static corrosion tests in organic coolants have been carried out in the Euratom Laboratories at Ispra, and under contract, in the Laboratories of Progil (France), Istituto Sperimentale dei Metalli Leggeri (Italy) and Tréfileries et Laminoirs du Havre (France).

Sintered aluminium powder product of different types, carbon steel, stainless steel, magnesium, beryllium and niobium have been tested between 400° and 450°C, in autoclaves and pyrex capsules containing a mixture of terphenyls. Exposure times ranged from 24 to 2000 hours. The influence of additions of water, oxygen and chlorine has been studied.

Sintered Al, steels and Be show a good resistance to pure terphenyls, Mg is heavily oxidized and Nb can be severely hydrided. Water additions accelerate iron corrosion and chlorine enhances the corrosion of both carbon and stainless steels.

M ORGEL is the name given to the heavy water moderated, organic liquid cooled power reactor concept selected for study by Euratom.

1. INTRODUCTION

One of the most important problems related to the construction of a nuclear reactor is the knowledge of the behaviour of structural materials in the heat transfer medium. Although the behaviour of such materials in water, steam or in special gases is fairly well known, comparatively few data exist on the corrosion of these materials in non-electrolytic liquids. In the ORGEL project (development of an organic cooled heavy water moderated natural uranium reactor), corrosion studies in the organic coolant are therefore essential.

This report is a summary of the work carried out and of the results achieved up to date in the first stage of these studies concerning static tests without irradiation. The work described here was carried out in the metallurgy and physical-chemistry laboratories of the Euratom Centre for Research at Ispra (Italy) and, under contract, in the laboratories of Progil (France), Istituto Sperimentale dei Metalli Leggeri or "ISML" (Italy) and Tréfileries et Laminoirs du Havre or "TLH" (France).

2. MATERIALS

2.1 - The Organic Liquid

The liquid coolant chosen for the ORGEL program is a mixture of the three isomeric terphenyls, whose chemical formulas are given in Fig. 1. Liquids of this kind have already been studied in American reactors and are mostly known under the name of Santowax (product of Monsanto Company). The reference liquid for the ORGEL project contains about 15% ortho, 80% meta and 5% para-terphenyl. It is produced by Progil under the name of Terphenyl OM2. At room temperature, it is a solid, slightly yellow, waxy material, which melts at about 80°C. Some of its physical properties are given in Table 1 (1). The vapour pressure of OM2 is plotted as a function of temperature in Fig. 2, which shows that at 400°C (752°F), the vapour pressure reaches about 2 atm. (28.45 psi).

Remarkable progress has been made during the last few years in the production of the terphenyls and in the control of impurities. Nevertheless, some impurities are always present and as the pure organic liquid is relatively inert to most materials, they are responsible for most of the corrosion effects, even when present in amounts of the order of a few parts per million. The most important impurities in connection with this study are given in Tab. 2. No value is given for the total oxygen content as, up to now, no precise methods of analysis have been developped.

In our tests, these analytical values were accepted and no regular independent control of the variables was maintained, though occasional analyses were made as spot checks.

Special attention was paid to the chlorine content, following a discovery that it was for a short time as high as 60 ppm. Normally, it was of the order of 5 ppm.

From the beginning, the water content of the organic liquid was taken into particular consideration. Water present in terphenyls, after contact with moist air, may range from 100 to 200 ppm. However, it can be reduced to less than 10ppm by boiling the terphenyl under vacuum.

For a large number of tests, known amounts of water were introduced in the corrosion capsules. The actual water concentration in the liquid phase is not known with precision. Water solubility in terphenyls, and consequently partition coefficients for the liquid and vapor phase, have been determined only for relatively high concentrations of water and for lower temperatures than in our case (2).

A rather limited study to determine these relations, carried out by Progil, shows that in the conditions in which our tests were done, about half of the total water went into the liquid phase (3).

2.2 - The metals

The metals tested in the organic liquid described above are :

- sintered aluminium powder products of different qualities, with alumina contents up to 10%, as :
  - SAP, fabricated by ISML, main impurities : Fe 0.3% ; Si 0.15%; Cu 40 ppm; Mn 40 ppm;
  - FRITTOXAL, fabricated by TLH, main impurities : Fe 0.4% ; Si 0.13% ; Cu 0.01% ; Zn 0.02%

- magnesium, in the form of the alloy Magnox A 12 (Al 0.81% ; Be 50 ppm ; Mn 20 ; Cu 4.4 ; Na 12.8 ppm) ;
- beryllium, sintered, extruded, furnished by Pechiney, quality -110, with BeO : 9000ppm ; Fe : 350ppm ; Ni : 100ppm ; Al : 200ppm ; Cu : 50ppm ; C : 200ppm.
- niobium, commercial purity, furnished by Metallwerke Plansee
- carbon steel (A 37) , P+S 0.1%
- austenitic stainless steels of the Cr-Ni type, mainly the type NSMC of Ugine (12%Ni, 17% Cr, 2.3% Mo, 0.08% C)

The main emphasis has been put on sintered aluminium powder products and steels. Samples were tested after degreasing in acetone or after special surface treatments indicated below.

3. EXPERIMENTAL METHODS

Mainly, two types of tests have been carried out : tests in stainless steel autoclaves (500 to 5000 cm^3 capacity), and tests in glass capsules (pyrex, usually, about 45 cm^3 volume, containing 25 g. of terphenyl).

With the first type of test, several samples can be tested together, up to very long exposure times. With the second one, proper and clean test conditions are much easier to maintain and a reaction of the organic with the container material is eliminated.

One important drawback, that brings considerable limitations to the capsule method is the low resistance of the glass to internal pressure arising from the pyrolisis of the organic liquid. At 400°C tests lasting more than 2000 hours have been carried out. At 450°C several explosions occurred in about 300 hours, so that the duration of the tests had to be restricted to about 250 hours.

Most samples tested in glass capsules had a surface of 10 to 15 cm^2. The terphenyl was carefully degassed before sealing the capsules. In a part of the tests known amounts of water were added to the terphenyl by introducing into the capsules small calibrated glass capillaries filled with degassed water. One end of the capillary tube was open : water could be pumped out to a desired level before sealing the capsules.

Corrosion has been studied by measuring the weight change, by analysing the metal released into the liquid and by microscopic investigation. The X-ray microanalyser was employed for special problems. Weighing was done on an analytical balance, reading the tenth of a milligram. Corrosion products were not removed before weighing. Iron and aluminium analyses were carried out by flame spectroscopy, using a Beckman DU apparatus (4). For water determinations the Karl-Fischer method was employed.

4. RESULTS

4.1 - The behaviour of sintered aluminium powder products

Experimental data published in the literature generally indicate that aluminium and its alloys, as well as sintered Al powder products, are only slightly attacked by organic coolants (5-12). There are, however, discrepancies and in some cases non-negligible corrosion effects have been reported (13, 14). It is not alaways clear why there is such disagreement among the published results, but in most cases, test conditions and purity of the organic liquid are not comparable and sometimes not even well defined.

4.1.1. Preliminary tests on SAP in autoclaves.

Preliminary tests on SAP carried out at ISML in a 500 cc stainless steel autoclave, yielded very poor results. After an exposure time of several days in OM2 at 400°C, the SAP samples (degreased before test in acetone), were found covered with a non-adherent, black coating and snowed a weight gain of more than 100 mg/dm^2. The photomicrograph of Fig. 3 shows a cross section of such a sample. Analysis of the peeled off coating showed mainly $\alpha . Al_2O_3$ (identified by X-ray diffraction) and about 2% of both iron and carbon.

X-ray microanalysis confirmed the prevailence of Al_2O_3 and demonstrated that the iron was concentrated (in the form of $Fe Al_3$), in the white inclusions, clearly visible in Fig. 3. This coating is therefore an actual corrosion product and is not due to a deposition from external source. Similar coatings have been observed in corrosion tests carried out at Progil, in mild steel autoclaves, which, on account of their

bottle-like shape, were difficult to clean. The nature of these coatings seems similar to that of the one observed by D. Buttinelli and G. De Gregorio (13, 14).

As the iron concentration was found to be higher in the coating than in the metal (where it is less than 0,3%), an interaction between SAP and the steel of the autoclaves was taken into consideration and a special study was started. Later on, it was found that if the SAP samples were etched with a sodium hydroxide solution and if the organic liquid was througly degassed, the formation of the coating could be avoided.

4.1.2. Tests on SAP in glass capsules.

Many more tests have been carried out at 400°C and 450°C in glass capsules, at the research laboratories of Progil, under the direction of J. Laporte and F. Giolito (3). Exposure times ranged up to 2000 hours and the organic liquid was changed several times without touching the samples when the temperature was 450°C. Many tests have been carried out with only one SAP sample in each capsule, while other capsules contained both samples of SAP and steel with or without electrical contact between them.

Generally there was very little corrosion. Weight changes of the order of a few mg/dm^2 were mostly positive and only sometimes negative, but hardly measurable on small samples of 10 to 15 cm^2 surface area. Because of the scatter in the results, no kinetic law could be established. The presence of stainless or carbon steel did not influence the corrosion of SAP in tests up to 1000 hours with dry or wet terpehnyl, at least when the surfaces were of comparable dimensions, as in our case. An oxygen cover gas had no effect on the samples. Water additions, however, enhanced the corrosion to a certain extent.

In Table 3 and 4 weight changes obtained in function of water addition and test duration at 400°C and 450°C respectively are reported.

Tests run in dry, clean terphenyl OM2, at 400°C and 450°C up to 500 hours, did not show any noticeable corrosion effect. Weight changes ranged normally around 1 mg/dm2 and the aspect of the samples was apparently not altered. Addition of 500 ppm of water (*) at 400°C gave the same result with no significant change, even after 2000 hours. At 450°C, the effect of 500 ppm of water was scarcely noticeable;after 1000 hours and after 2000 hours weight gains of about 5 mg/dm^2 were obtained, together with a faint discoloration of the surface. The addition of 2000 ppm of water, however, results in a considerable attack at 400°C (test at 450°C with such high water concentrations have not been run in glass capsules). Weight gains reached several mg/dm^2 after 1000 hours and even more than 100 mg/dm^2 were found on a sample of SAP 960 (4% Al_2O_3) after 2000 hours. These high weight gains correspond to severe local attack, which penetrated deeply into the sample, as demonstrated by Fig. 4.

Chlorine additions to the organic liquid also influence the corrosion of SAP. As may be seen in Table 5, weight changes are not significantly altered by chlorine and no reasonable relationship can be deduced between aluminium release into the liquid and chlorine content. However, the appearance of the samples reflects the presence of chlorine, even when it is present in the concentration of 20 ppm. As tests with smaller chlorine additions and longer duration have not been run, there is not yet an indication of a sensivity limit with respect to chlorine concentration.

(*) as indicated above, only about half the concentration is in the liquid phase.

For some tests at 450°C, terphenyl OM2, which had circulated for several months in a test loop and contained about 200 ppm of iron and 100 ppm of chlorine was used. Table 6 shows that this impure terphenyl led to high weight gains and to important deposits on the samples. Water additions considerably enhance weight gains. As the total amount of Al in the liquid before test was about 0.03 mg, the values of the last column show an important aluminium release. The discrepancy between the last two figures of this column does not allow a conclusion to be drawn, regarding the influence of water on this aluminium release.

The differences in the behaviour of the three SAP types tested containing respectively 4, 7 and 10% Al_2O_3, are normally very small (cf. Tables 3 and 4).
SAP 895 (10% Al_2O_3) seemed at first to be a little more sensitive to corrosion than the others. But this effect was apparent only in wet OM2 and on samples degreased and not etched; it probably does not depend on the alumina content. The influence of the surface treatment on corrosion behaviour is quite pronounced for SAP 895 and much less for the others. Unetched samples, with their surfaces of rolling or drawing being only degreased, are often covered during the corrosion experiment in wet terphenyls, with a dark brown layer and sometimes with many small pits. However, samples which had been etched in a sodium hydroxide solution, usually remained unchanged except for the formation of small streaks and sometimes very small pits along the extrusion lines.

4.1.3. Microscopical and microanalytical tests.

The small pits and the areas around them were studied in detail by Mr. R. Theisen, using the X-ray microprobe technique (15). Fig. 5 shows the aspect of such a pit after a careful slight

polishing procedure, where there is an inclusion clearly visible in the middle. Another of these inclusions is shown in detail in Fig. 6, with white points clearly visible in it. The microprobe analysis revealed that the matrix of the inclusion consists of $FeAl_3$ and that the white spots contain iron and aluminium in amounts corresponding to the formula $FeO \cdot Al_2O_3$.

The brown colored region mentioned above seems to correspond to the formula 2 $FeO \cdot Al_2O_3$ or possibly $Fe_2O_3 \cdot Al_2O_3$. The mechanism of formation of these products is not clear. The impossibility of microprobe oxygen analyses does not allow identification of the formulae with precision. In the inclusion itself traces of chromium and nickel are also detectable, indicating that the inclusion was most probably introduced during the powder preparation. The big inclusions are often surrounded by a large number of smaller ones, which produce upon corrosion a brown colouring of the sample.

Samples corroded in water at room temperature exhibit a much more evident local attack. The pits are often accompanied by large oxide eruptions. Fig. 7a shows the cross section of such a pit. The sample has been exposed to tap water for a month. In the middle of the pit there is an inclusion consisting, as shown by microprobe analysis, of $FeAl_3$. A scanning of the sample for Al $K\alpha$ radiation shows a darker circle representing a reduction of the aluminium concentration around the inclusion. Point analysis in this area revealed an Al concentration of only 18% and an iron concentration of about 0.3%, indicating formation of hydrous oxides. A scanning for Ni and Fe $K\alpha$ radiation demonstrated the presence of iron and nickel in the inclusion (Fig. 7b). It is thus clear that iron is principally responsible for the corrosion effects observed on SAP. There may perhaps be formation of galvanic couples at small distances even in the insulating liquid, where a layer of absorbed water can possibly act as an electrolyte.

The improvements in the corrosion resistance by the etching treatment with sodium hydroxide is explained by the removal of particles rich in iron. Wolf and Neunzig (16) have already reported a considerable reduction of the corrosion of aluminium in water by removal of the drawing surface containing impurities introduced by the production process. A similar effect seems quite probable for SAP in terphenyl. There is also the possibility that the hydroxide dissolves preferably the more corrodable regions and leaves a surface of greater resistance.

4.1.4. Tests on Frittoxal and Raffinal.

Tests on Frittoxal have been carried out by Mr. Lelong at TLH, in very clean conditions. The samples were placed in an alumina crucible inside the stainless steel autoclave and the terphenyl used had not been in contact with air from the time it was purified. No corrosion was observed and sometimes only a faint colouring of the surface occurred after an exposure time of 1000 hours at 450°C. No detailed microscopical analysis has however been done up to now.

For comparison, a few tests have been carried out on pure Al (Raffinal) in pyrex capsules at 400°C for 200 hours. The samples did not exhibit any significant sign of attack, even when 2000 ppm of water were added.

4.1.5. Summary.

Summarizing the results obtained, we may say that sintered aluminium exhibit a good corrosion resistance in terphenyls. Even in an organic liquid to which about 500 ppm of water(*) had been added, no significant increase in the corrosion has been found in 1000 hours at 450°C.

(*) see footnote, page 15

Local corrosion attack is caused by iron-rich inclusions, above all $FeAl_3$, but it does not seem to be critical. A prior etching with a sodium hydroxide solution improves the corrosion resistance of the samples by eliminating surface areas rich in impurities.

4.2 - The behaviour of steels

4.2.1. Carbon steel.

Carbon steel and low alloyed steels are envisaged as construction materials for the main part of the primary reactor circuit. Literature data on their corrosion in organic coolants (5,7,10,12) indicate generally more pronounced effects than have been found on aluminium. A detailed knowledge of the extent of this corrosion turns out to be most important on account of the fact that the fouling deposits formed on heat transfer surfaces (fuel elements) contain iron as their main metallic constituent. This iron is set free by the corrosion processes and carried by the liquid to hot surfaces where it deposits preferentially. It is for this reason that corrosion studies under conditions nearest to those of the ORGEL project were considered necessary. Up to now, however, the study has been limited to tests in glass capsules on carbon steels at Progil (tests with low alloyed steels in autoclaves are being prepared at Ispra). Weight changes and the amount of iron released to the liquid were determined. The iron analysis was done by flame spectroscopy. As part of the iron was deposited on the walls of the glass capsule, care was taken to include a determination of this iron as well.

In dry terphenyls, practically no corrosion of mild steel has been observed. However, at 400°C, water and oxygen additions may cause significant weight gains. Examples are given in Table 7 for tests up to 500 hours. With 500 ppm of water, an increase in weight of about 4 mg/dm^2 has been found after 1000 hrs. and about 6 mg/dm^2 after 2000 hours.

With 2000 ppm and at the same temperature, weight gains up to 18 mg/dm^2 and 22 mg/dm^2 were observed for 1000 and 2000 hours respectively.

After 2000 hours, at 450°C with 500 ppm of water, weight gains are even higher, being between 60 and 90 mg/dm^2. In Table 8 some values for different conditions are reported.

Results of tests with an oxidized terphenyl, obtained by bubbling oxygen through boiling OM2 for 8 hours, are given in Table 9. As can be clearly seen, this treatment enhances corrosion. The influence of chlorine is shown in Table 10. For these tests, chlorine had been added as $C_6H_6Cl_6$. In spite of a considerable scatter, the detrimental effect of chlorine is evident when its concentration exceeds 10-15 ppm. An example of the effect of surface treatment is given in Table 11. Obviously, the iron release is enhanced by a previous nitric acid etch. The weight gain data do not differ very much ; one high value appears however just for the etched sample.

Considering the figures at 500 hours in Table 7 as representative values, one can deduce that for dry terphenyls weight gains are of the order of 1 mg/dm^2 month. Assuming that the whole weight gain is due to the oxidation of Fe to Fe_3O_4 (*), it can be presumed that about 2,5 mg of iron are oxidized per dm^2 per month. Iron release to the liquid has not been measured in this case, but it may be assumed that it is around 0,5mg/dm^2/month, so that the total metal loss amounts to about 3 mg/dm^2/month. On the basis of this figure, the loss in wall thickness can be calculated to be about half a micron per year, assuming linear oxidation and uniform attack. From a mechanical point of view this is absolutely insignificant.

(*) X-ray diffraction analysis carried out at Ispra by D. Quataert, show only this corrosion product.

With 500 ppm of water (*), weight gains of about 6 mg/dm^2 have been found after 2000 hours at 400°C. Iron release is valued to be about 1 mg/dm^2/month. Consequently, about 7 mg/dm^2/month of iron are oxidized, which corresponds to a thickness loss of about 1 μ per year. However, at 450°C, values about 10 times higher may be reached.
For 400°C, the order of magnitude of the values reported corresponds to those given by Parkins (11). On the basis of loop tests with a circulating organic coolant containing from 100 to 200 ppm of water, Parkins estimates a corrosion rate of 6 mg/dm^2/month for carbon steel and low alloy steels in organic coolants, at 316°C (600°F). He considers that these values may be lower if the water and oxygen contents are lowered.

It may be concluded that for the case of the primary circuit of an organic cooled reactor, the corrosion of carbon steels in organic liquids is not a problem, as far as the metal itself is concerned ; but, owing to the very large surfaces in contact with the liquid, the amount of corrosion products released into the liquid may be critical.

4.2.2. Stainless steels.

According to the literature (5-10), stainless steels exhibit a good corrosion resistance in terphenyls and similar liquids. The first corrosion tests on SAP, however, gave rise to the suspicion that stainless steels may influence the behaviour of SAP. Consequently, a series of tests were started, as described earlier (pyrex capsules, 400°C and 450°C). The samples were usually passivated by nitric acid, as it had been stated that this treatment sometimes led to a lesser extent of surface coating than did polishing on emery paper.

(*) see footnote, page 15

In most cases, there was a weight gain, but sometimes, especially in the presence of chlorine, a weight loss. The iron release varied without relation to the weight change, except when much chlorine was present.

In dry terphenyls, weight gains and iron release were of the same order of magnitude as for carbon steel, i.e. often at the limit of the sensivity of the balance (0.1 mg). At 400°C water additions up to 500 ppm (*) produce nearly the same effects for both carbon and stainless steels for short test durations. (cf. Table 12 and Table 7). For periods of more than 1000 hours in the same conditions, stainless steel, however, corrodes more slowly.

At 450°C, 500 ppm of water, the difference between the two materials is quite obvious : whereas stainless steels gained about 10 mg/dm^2 after 1000 as well as after 2000 hours, the corresponding figures for carbon steel were around 40 and 75 mg/dm^2 respectively. The surface of the stainless steel samples remained smooth, brown coloured, whereas the carbon steel surface showed a rough, brittle black coating, parts of which could be easily removed. Table 13 gives some weight changes for different conditions.

The effect of chlorine content in the organic liquid is quite obvious. During a certain period, the liquid contained between 20 and 60 ppm of chlorine which were not detected. Weight losses were found to be much more frequent during this period than during others, when the chlorine concentration ranged between 3 and 8 ppm. The effect of chlorine is shown quite clearly by the figures of Table 14, reporting the results of a short time test at 450°C. No attempt has been made to compare fully the different types of austenitic steels. Short time tests showed that the behaviour of a series of austenitic steels was quite similar. No conclusions can be drawn about long time behaviour, however.

(*) see footnote, page 15

The fact that even when water is present there is only little iron release seems to indicate that a protective coating, stable in the absence of chlorine, is formed. The presence of chlorine is detrimental. As indicated in the literature, there is no doubt that stainless steels have a better long time behaviour than mild steels.

5. THE BEHAVIOUR OF OTHER METALS

5.1 - Magnesium

Magnesium oxidizes readily at high temperature. However, because of its very interesting nuclear properties (low neutron absorption) it seemed worthwhile to study its behaviour in terphenyls. Tests have been carried out in stainless steel autoclaves, on the alloy Magnox A 12, by G. De Beni at Ispra. The results were quite unfavourable.

At 400°C in terphenyl OM2 containing 5 ppm of water, weight gains of 25 and 250 mg/dm^2 were found after 100 and 400 hours respectively. At the same temperature, with a liquid containing 200 ppm of water, however, weight losses of about 60 and 300 mg/dm^2 respectively were observed. Removal of the corrosion product brought these values to about 240 mg/dm^2 and 1.5 g/dm^2.

At 450°C, obviously, a reaction between magnesium and oxygen containing compounds dissolved in the terphenyl takes places. The extent of oxidation in "dry" terphenyls is greater than what could be estimated considering the traces of water still present. About 600 mg/dm^2 have been lost after 100 hours in terphenyl OM2 containing 5 ppm H_2O, the corrosion product being MgO.

In agreement with the literature, our results indicate that no applications exist for magnesium in contact with terphenyls at the envisaged reactor temperature.

5.2 - Beryllium

Only limited data are available in the literature on beryllium behaviour in terphenyls (4,9,10,11). A few tests have been carried out by Progil. Cylindrical samples, which were tested in pyrex capsules at 400°C for 1000 hours, showed weight gains of 1 mg/dm^2 and 5 mg/dm^2 for dry (<10 ppm water) and wet (500 ppm water) OM2 respectively. For an exposure time of 300 hours at 450°C, the corresponding weight gains were 4 and 10 mg/dm^2. The samples showed only a slight brown colouration but no signs of attack.

5.3 - Niobium

For niobium, the data available in the literature are also very limited (10,11,12). It is not specified whether the weight gains are due to oxidation or hydrogen pick up. For this reason, some experiments were carried out at the C.C.R. Ispra, by Mrs. F.Coen. Slabs of two different thicknesses (1.5 and 0.025mm) were exposed in glass capsules, between 400°C and 450°C to dry and wet (up to 200 ppm H_2O added) terphenyl OM2. Hydrogen pick up was determined by gas extraction at 1500°C; weight gains could be determined only for the thick samples, as the thin ones became so brittle that they broke into small pieces.

The thick samples, in a test of 336 hours at 400°C, picked up between 35 and 55 ppm of hydrogen and showed weight gains of about 0.3 mg/cm^2. About 10 to 20% of the weight gain was due to hydrogen uptake. No relationship to the water content could be deduced.

The thin samples, tested for 190 hours at 410°C reached hydrogen uptakes as high as 3000 ppm. Considering the higher surface to volume ratio of these samples, it appears, however, that hydrogen penetration of the surface is of the same order of magnitude as for the thick ones.

A temperature rise resulted in a much higher hydrogen uptake. After 190 hours, 1000 to 3000 ppm were found for the thick samples at 450°C and about 7000 ppm for the thin samples at 435°C. For the thick samples in this case, at least half of the weight gain was due to hydrogen uptake. The samples generally did not show any change in appearance, except an occasional faint blue coloration. The big temperature dependance of the hydrogen uptake is not necessarily due to a higher hydrogen sensibility of the metal, but it is probably related to the higher hydrogen pressure in the capsules, as the pyrolisis of the organic is at 450°C much fatser than at 400°C.

ACKNOWLEDGEMENTS

This report is based on the work of different laboratories. Thanks are expecially due to Mr. Laporte and Mr. Giolito (Progil), Mr. Gualandi and Mr. Luft (ISML), Mr. Herenguel and Mr. Lelong (TLH), who worked under contracts and to Mrs. Coen, Mr. Jehenson, Mr. Theisen and Mr. De Beni, of EURATOM's C.C.R. Ispra.

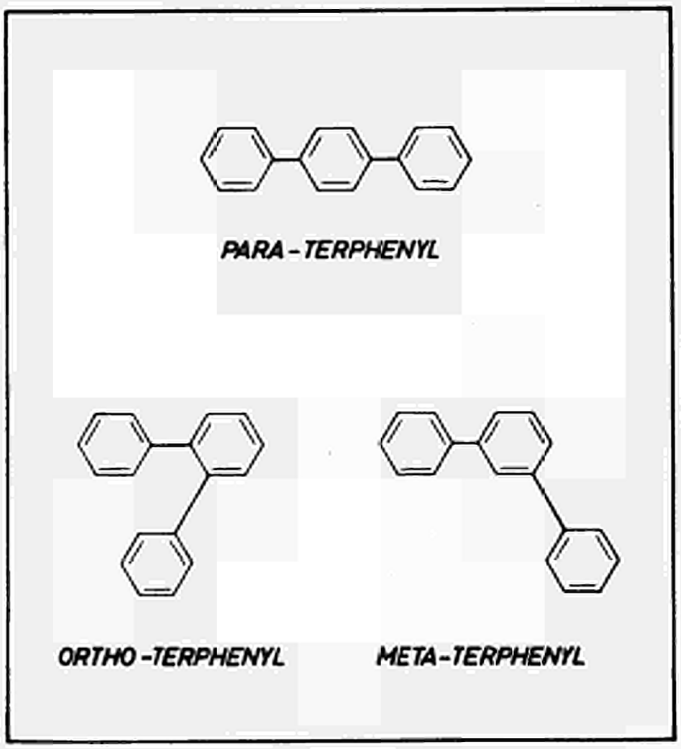


Fig. 1 — The three terphenyls

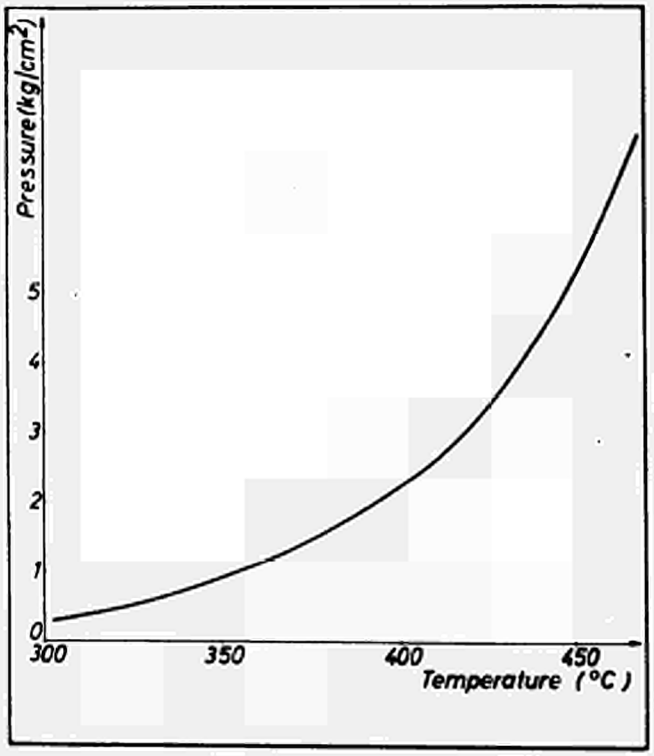


Fig. 2 — Vapour pressure of Terphenyl OM2 as given by Progil (1)

Fig. 3 — SAP corroded for 20 hrs. at 400° C in terphenyl OM2 in a stainless steel autoclave. x 1000

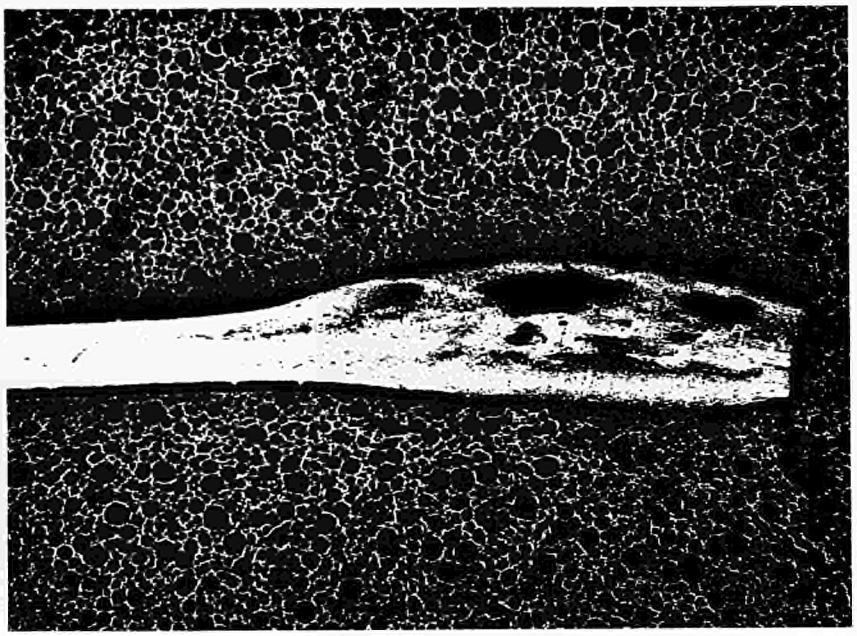


Fig. 4 x 11
SAP 960 corroded during 2000 hrs. in terphenyl OM2 with 2000 ppm of water at 400° C

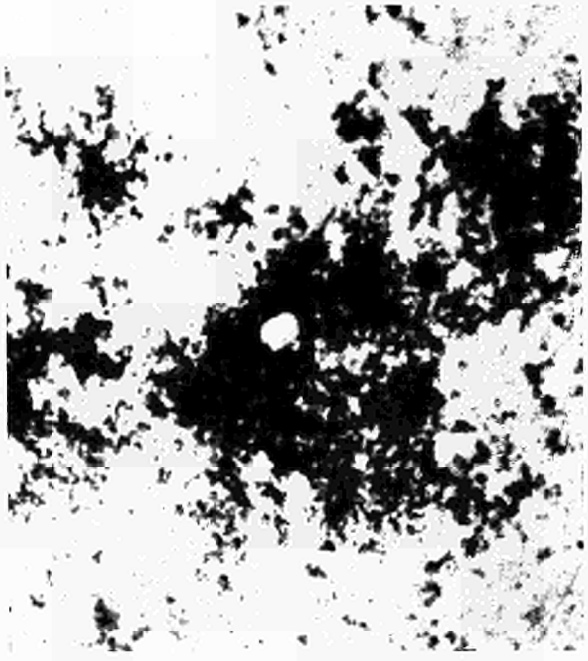
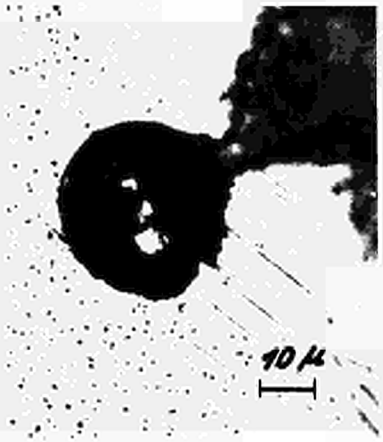


Fig. 5 x 500
Local corrosion on SAP 895 in terphenyl OM2 (26 hrs., 450° C, 1 mm. O_2)

Fig. 6 x 500
Inclusion in a corroded sample of SAP (same conditions as in Fig. 5)



a) Optical Micrograph

Al $K\alpha_1$

Fe $K\alpha_1$

b) Scanning Pictures

Ni $K\alpha_1$

Fig. 7 — Microanalysis of SAP 960 corroded in tap water

TABLE 1

Properties of Terphenyl OM2

Composition :

ortho-terphenyl	14-16%
meta-terphenyl	79-81%
para-terphenyl	3-5%
diphenyl	< 1%

melting point	~ 80°C (176°F)
boiling point	357°C (675°F)
density at 200°C	0,96 g/cm^3
at 400°C	0,80 g/cm^3
viscosity at 200°C	0,9 cp
at 400°C	0,24 cp
temperature of self-ignition	> 500°C (932°F)

TABLE 2

Impurities in terphenyl OM2 as given by Progil

H_2O	in the order of 50 ppm
Cl	< 8 ppm
Fe	1-2 ppm
Al	< 1 ppm
S	30-40 ppm

TABLE 3

Weight changes (mg/dm^2) of SAP at 400°C

A : SAP 960 (4% Al_2O_3)
B : SAP 930 (7% Al_2O_3)
C : SAP 895 (10% Al_2O_3)

Water added ppm	200 hours	500 hours	1000 hours	2000 hours
0	A +1.3 +0.7 B +0.6 -0.6 +0.7 +0.7 C +1.3 +0.7	C +5.3 0 +0.6 -1.3 +2.1 +2.1		
500	B 0 -0.6	C -0.6 +1.3 0 -0.6 +2.1 +2.8	A 0 -0.5 0 -1.1 B -2.5 0 +2.1 0 0 +2.7 +6.6 +5.4	A +1 0 +1.1 +1.1
2000			A +4 +8 +2.5 +8.7 +8.3 +19.4 +7.5 +7 B +6 +4.7 C -2.7 +2	A +47 +130 +17 +13

TABLE 4

Weight changes (mg/dm^2) of SAP at 450°C

A : SAP 960 (4% Al_2O_3)
B : SAP 930 (7% Al_2O_3)
C : SAP 895 (10% Al_2O_3)

Water added ppm	200 hours	333 hours	1000 hours	2000 hours
0	B +2.6 +1.3 C +1.3 +2.1 +0.7 +1.3	C +2 +1.3		
500	A +2.6 +2.6 B +3.3 +2 +1.3 +2.1 C +2.8 +2.8 +2.6 +1.3 +1.3 +2.6	C 0 +3.4	A +5 -3.3 +4.1 B +8 +10 +1.3 -0.6	A +12 +5

TABLE 5

Corrosion of SAP 960 in dry terphenyl OM2 containing different amounts of chlorine

231 hrs. - 450°C - (Cl added as $C_6H_6Cl_6$)

Samples Nr.	Cl added ppm	Δ P mg / dm^2	Al found in liquid ppm	OBSERVATIONS
A 72	-	+ 1.3	.65	Faint brown pits
A 73	-	+ 1.3	.35	Practically unchanged
A 74	20	0	.62	Important attack
A 75	20	+ 2	1.7	Brown pits, dark grey areas
A 76	50	+ 1.3	7.9	Dark grey, numerous pits
A 77	50			Very dark, brown pits
A 78	100	+ .71	.45	Brown pits
A 79	100	+ 1.3	.6	Black points surrounded by white areas

TABLE 6

Corrosion of SAP 960 in terphenyl containing about 200 ppm Fe and about 100 ppm Cl - 192 hrs. - 450°C

SAMPLE Nr.	H_2O added ppm	Δ P mg / dm^2	Al content in liquid (total) mg.	OBSERVATIONS
A 68	-	+ 23.3	.49	Unchanged grey colour but large black areas
A 69	-	+ 54	.78	Grey areas, black deposits
A 70	500	+ 160	.31	One side dark grey, other side areas of bright and dark grey colour
A 71	500	+ 156.5	2.7	Very dark grey with brighter area

TABLE 7

Corrosion of carbon steel in terphenyl OM2 with additions of water and oxygen at 400°C

Duration hours	Water added	Oxygen cover gas	Δ P mg/dm^2	iron in liquid ppm	OBSERVATIONS
200	-	-	.6	2.4	Unchanged
200	-	-	.6	1.4	"
238	500	-	2.4	5.5	Brittle black coating
238	500	-	4.7	3.8	"
238	-	+	9.1	6.1	"
238	-	+	8.8	6.8	"
238	500	+	6.8	7.4	"
238	500	+	8.9	7.4	"
500	-	-	.6	n.d.	Unchanged, some black areas
500	-	-	.6	n.d.	

TABLE 8

Corrosion of carbon steel in terphenyl OM2

at 400°C and 450°C

Weight changes (mg/dm^2) at 400°C

Water added ppm	200 hours	500 hours	1000 hours	2000 hours
500	+4.6 +3.3 +2.7 +5.3	+2 -2.6 +2.6 +1.3 +0.6 +0.6	0 +2 +1.3 +1.3 +4.0 +2.0	+5.2 +6.7 +3.3 +2.0 +6.7 +4.0
2000			+3.3 +18 +15 +15	+14 +22 +15 +21

Weight changes (mg/dm^2) at 450°C

Water added ppm	200 hours	333 hours	1000 hours	2000 hours
500	+4.7 +2		+38.7 +31.4 +42.7 +42.7	+90 +62 +53.5

TABLE 9

Corrosion of carbon steel in oxidized terphenyl

200 hrs. - 450°C
(samples cleaned with a metallic brush before test)

Sample Nr.	Water added ppm	ΔP mg/dm^2	Fe ppm	OBSERVATIONS
1024	-	5.3	2.4	Thin coating
1025	-	5.3	0	
1026	500	9.3	0.8	Black coating
1027	500	14.6	0	

TABLE 10

Influence of chlorine on the corrosion of carbon steel

450°C - 200 hrs.

Sample Nr	Cl ppm	Δ P mg/dm^2	Fe ppm	OBSERVATIONS
1023	2	- 1.3	0	Brown pits
29	2	- 3.3	1	Unchanged
30	5	+ 2.6	0	Unchanged
31	5	+ 1.3	0.6	Unchanged
32	10	+ 3.3	5.2	Brown pits
33	10	0	3.3	Unchanged
34	15	+ 8	5.4	Coated areas and some pits
35	15	+ 3.3	0	

TABLE 11

Influence of surface treatment on corrosion of carbon steel in dry terphenyl

113 hrs. - 400°C

Preparation	Δ P mg/dm^2	Fe in liquid ppm	Observations
Emery paper	0.7	1.7	Faint brown colour
"	0.6	1.7	"
HNO_3 25%	0.6	4.7	Unchanged
"	2.0	3.7	"
Metallic brush	0.6	1.3	"
"	0.6	3.3	"
Polishing cloth	0.6	1.2	"
"	0.6	1.8	"

TABLE 12

Influence of water on the corrosion of austenitic stainless steel at 400°C in terphenyl OM2

Duration hrs.	Water added ppm	ΔP mg/dm^2	Fe in liquid (ppm)	Observations
206	-	0,5	2.4	Unchanged
206	-	0,9	3.1	"
206	-	0.5	3.3	"
206	-	0.5	3.6	"
206	500	0.9	3	Faint brown colour
206	500	2.4	3.5	"
206	500	0.9	3	"
206	500	2.9	3.7	"
501	-	1.8	3.7	Very faint brown colour
501	-	1.4	3.9	"
501	500	1.9	2	Faint brown colour
501	500	3.7	2.3	"

TABLE #13

Corrosion of stainless steel in terphenyl OM 2

at 400°C and 450°C

Weight changes (mg/dm^2) at 400°C

Water added ppm	200 hours	500 hours	1000 hours	2000 hours
500	+1.3 +3.3 +1.3 +4	-0.6 0 +4.2 +4.2 +2.3 +5.5	+6.6 0 +1.3 0 0 +2.1	+2.7 +4 -0.7 -2.7
2000			+12.5 +11.5	+14 +14

Weight changes (mg/dm^2) at 450°C

Water added ppm	200 hours	333 hours	1000 hours	2000 hours
500	+8 +8	+8 +9.3	+10 +7 +10	+11

TABLE 14

Influence of chlorine on the corrosion of stainless steel in terphenyl OM2

24 hrs.- 450°C

Preparation : 1. emery paper, then etching and passivation (HNO_3)

2. idem, but without polishing on emery paper

H_2O added (ppm)	Cl ppm	preparation	Δ P mg/dm^2	Fe in liquid (ppm)	Observations
-	3	1	+1.5	2.5	Unchanged
-	"	1	+1.7		"
-	"	2	+0.9	2.1	"
-	"	2	+0.4	4.1	"
-	100-200	1	-30.5	148.9	Continuos dark coating
-	"	1	-31.2	112.7	"
-	"	2	-21.2	25.5	"
-	"	2	-11.8	49.2	"
500	3	1	+1.9	0	Thin brown coating
"	"	1	+2.3	3.3	"
"	"	1	+2.0	2.4	"
"	"	1	+1.9	1.8	"
"	100-200	1	-22	23.1	Heavy coating
"	"	1	-32.6	207.7	"
"	"	1	-23.3	16.2	"
"	"	1	-18.7	58.8	"

REFERENCES

(1) Sté PROGIL, Organic fluids as moderators and heat-transfer agents for the nuclear energy, Paris, Oct. 1962

(2) H. MANDEL, NAA-SR-Memo-4753 (1959)

(3) F. GIOLITO, Final Report on work under EURATOM Contract 028-61-5 ORGF (in the press)

(4) PROGIL - EURATOM Contract 006-60-10 ORGF

(5) G.C. MILAK, ANL-5587 (1956)

(6) W.C. BOYD et al., BMI-1160 (1957)

(7) H.E. DAVIES, AERE M/M 153 (1957)

(8) N.J. GIOSEFFI and M.E. KLINE, NAA-SR-2570 (1959)

(9) H.E. KLINE and J.C. COCHRAN, NAA-SR-5350 (1960)

(10) G. ITO et al., Conference on Corrosion of Reactors Materials, Salzburg, June 1962 (CN-13/9)

(11) W.A. PARKINS, Conf. on Corrosion of Reactors Materials, Salzburg, June 1962 (CN-13/15)

(12) R.S. NEYMARK and J.L. BALLIF, NAA-SR-7400 III-E-1 (1962)

(13) B. BUTINELLI and G. DE GREGORIO, La ricerca scientifica, Vol.I part II (2), 123 (1961)

(14) D. BUTINELLI and G. DE GREGORIO, Metallurgia Italiana, 50 - (5) 165, (1962)

(15) R. THEISEN, Rev. Metallurgie, (in the press)

(16) H. WOLF and H. Neunzig, Aluminium, 26, 17 (1944)

CDNA00379ENC